Synthesis and Characterization of C60_aza_BODIPY:
UROP Project Review

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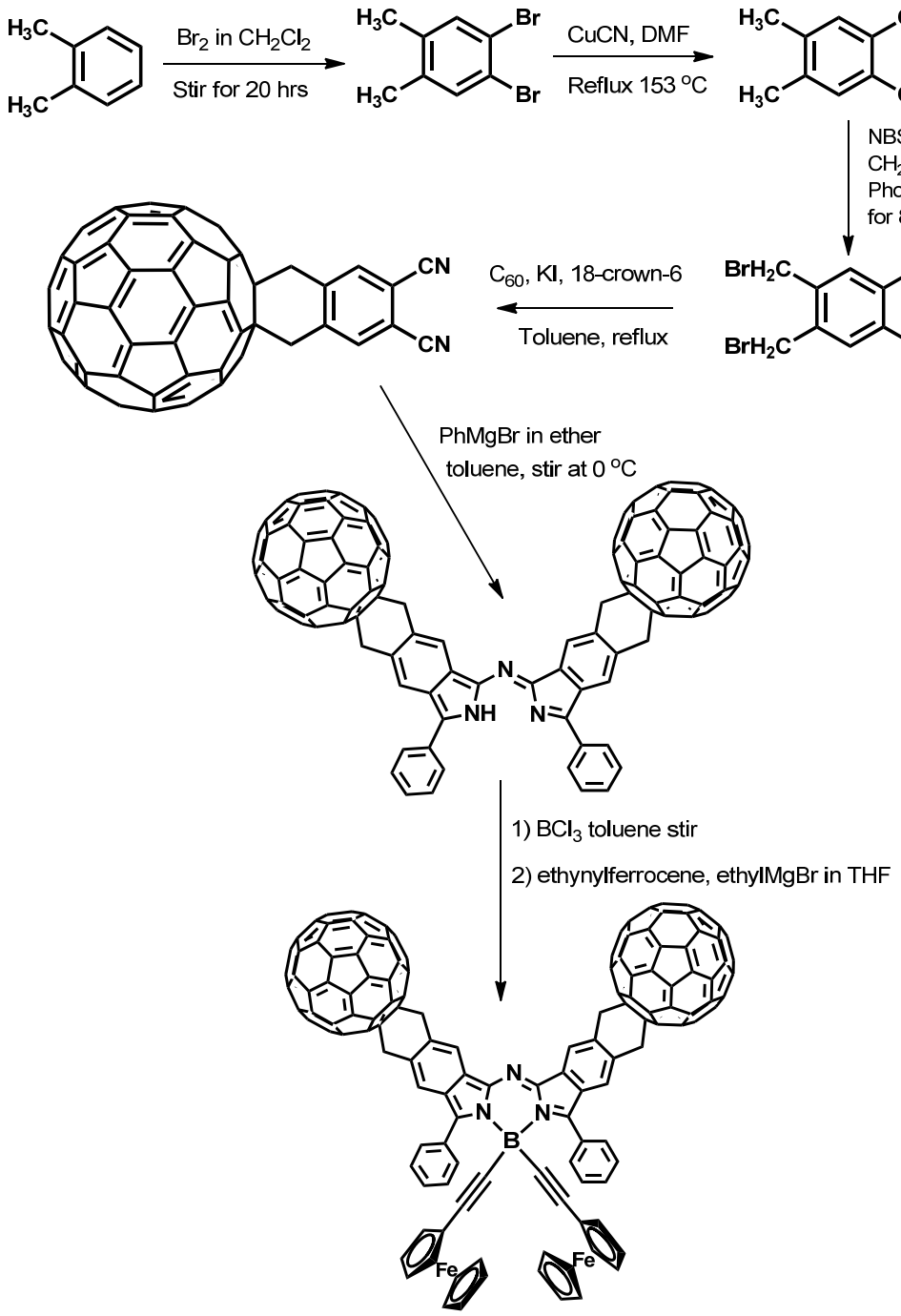
The goal of this project was to learn lab techniques and to construct a multi-modular donor-acceptor pentad to apply to research in molecular solar energy harvesting using porphyrins. The basic component of this type of complex is the photo-induced charge separation state of the supramolecular system that allows for efficient conversion of solar energy (photons) into chemical potential. Some variables of these systems include the distance from the electron donor to electron acceptor and the orientation of these donor-acceptor components (Wasielewski, 1992). It has been found that porphyrins and phthalocyanines are useful to these systems because of the light-absorption properties and how the free electrons behave in these complexes.

In order to be able to use this C60_aza_BODIPY for the capture and storage of electricity, a series of chemical reactions is needed to prepare the supramolecule as a closed circuit that can contain free electrons ejected from their orbitals instead of losing them to the surroundings or replacement into the molecular orbitals. Phthalocyanines are aromatic compounds with large delocalized 18π electron systems. Aromaticity is an important concept in chemistry, describing the unusual stabilization of compounds with empty valence orbitals. This causes a lack of reactivity that is very uncharacteristic of compounds with empty orbitals that would like to be filled. It is postulated that this property is due to alternating carbon-carbon double bonds which allow electrons to freely pass around the aromatic ring and thus constantly find the most stable position without the need for outside electrons.

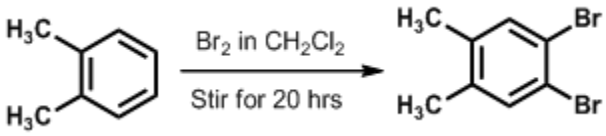
In this scheme, I was unable to construct the final molecule – I got as far as the formation of dicyano_o-xylene. I did work on C60-vis-dimethylphthalonitrile (the fourth step in the reaction series) with Dr. Maligaspe, but he had worked alone on the third step, the formation of 4,5dicyano-dibromoxylene, so my work on the reaction series was fragmented. In this paper, I will address the specific reactions performed, methods used, purification techniques, characterizations, and set-backs.

The complete synthetic scheme for the formation of C60_aza_BODIPY is as follows:



This schematic drawing is courtesy of Dr. Eranda Maligaspe.

The first reaction performed was the bromine substitution reaction in which bromine is attached to o-xylene in the presence of Fe and I_2 in DCM.



The initial ortho-xylene was made by a previous student and the remaining compound was confirmed by NMR spectroscopy:

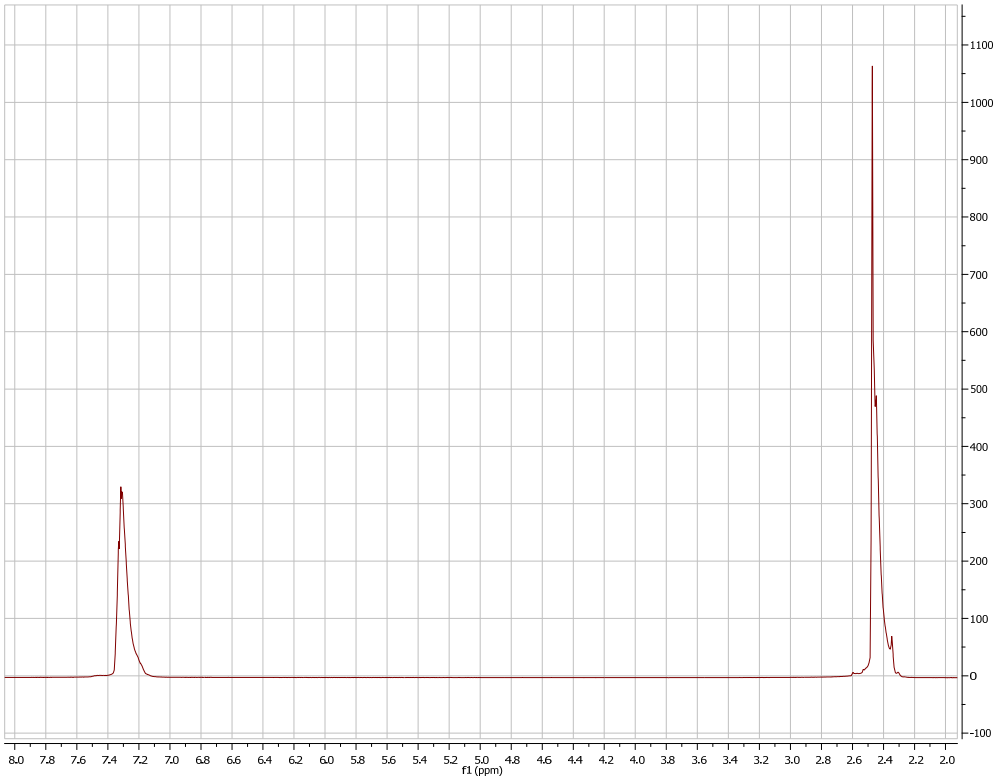


Figure 1. ^{1}H NMR confirmation of the presence and purity of ortho-xylene.

The reaction flask for the formation of dibromo_o-xylene was purged with Ar to eliminate any oxygen and moisture, after which all reactants besides Br_2 were added: 4 mL (33.15 mmol) o-xylene, 92.6 mg (1.66 mmol) Fe, 420.7 mg (1.66 mmol) I_2, and 110 mL DCM. 4.247 mL (82.89 mmol) Br_2 was added to a dropper with 30 mL DCM and the solution was added dropwise to the reaction flask over the course of 2 h. The reaction was cooled, kept at 0°C for 2 h, and stirred under vacuum for 40 h. Fe and I_2

were used as catalysts. Fe is a good catalyst because it is easily oxidized. I_2 is useful to this reaction because it absorbs photons in the region larger than 600 nm and produces few unwanted byproducts. This reaction was attempted several times with different proportions of reactants and catalysts with gradually increasing proportion of molecular bromine and more DCM. The formation of dibromo_o-xylene is light-sensitive – the product tends to break down under light exposure – so the entire reaction vessel is covered with aluminum foil and the light is turned off.

Workup:

1. Water Wash:

A solution of 10% NaOH was made by dissolving 10 g NaOH in 100 mL H_2O and then mixed with the bromination compound in a separatory funnel. The excess bromine attaches to the NaOH in the water layer, and the compound stays dissolved in the organic layer of DCM which, being more dense than water, separates out and is collected from the funnel. This process is repeated three times, or until there is no orange-brown color left to the compound in DCM (which should be a pale yellow). The dibromo_o-xylene is collected in three fractions (including the transition layer), from which the DCM is evaporated. The remaining compound is still a viscous liquid, which we believe to be caused by unreacted o-xylene.

2. Crystallization:

To crystallize the compound, the RB is heated with a heat gun – not too hot or the compound will break down – and ~6 drops hexane is added in order to encourage crystal growth. Hexane is chosen because, like the dibromo_o-xylene, it is nonpolar, and when heated and mixed with the slushy product, crystals form. The top of the flask is covered to reduce interaction with outside particles and placed in the fridge overnight. Quick cooling further encourages crystal growth.

The crystals are collected the next day if they had formed. Oftentimes there would be some crystals formed still in a yellow solution. Sometimes no liquid was left, and sometimes no crystals had formed whatsoever. This issue caused significantly low product yields, which was why this reaction had to be performed several times and slowed our progress to the final compound.

3. Extraction:

A B-funnel was prepared with a filter flask connected to a vacuum. The wet crystals are placed on the filter paper and the vacuum is started, sucking out the excess o-xylene and drying the crystals. A small amount of the dried compound is tested with hexane to make sure that it doesn't dissolve. If the crystallized product doesn't dissolve, it is rinsed with hexane on the filter paper with the vacuum going and then completely dried. From the reaction amounts listed above, the reaction yielded 1.312 g (4.97 mmol) dibromo_o-xylene. The compound was confirmed by NMR spectroscopy:

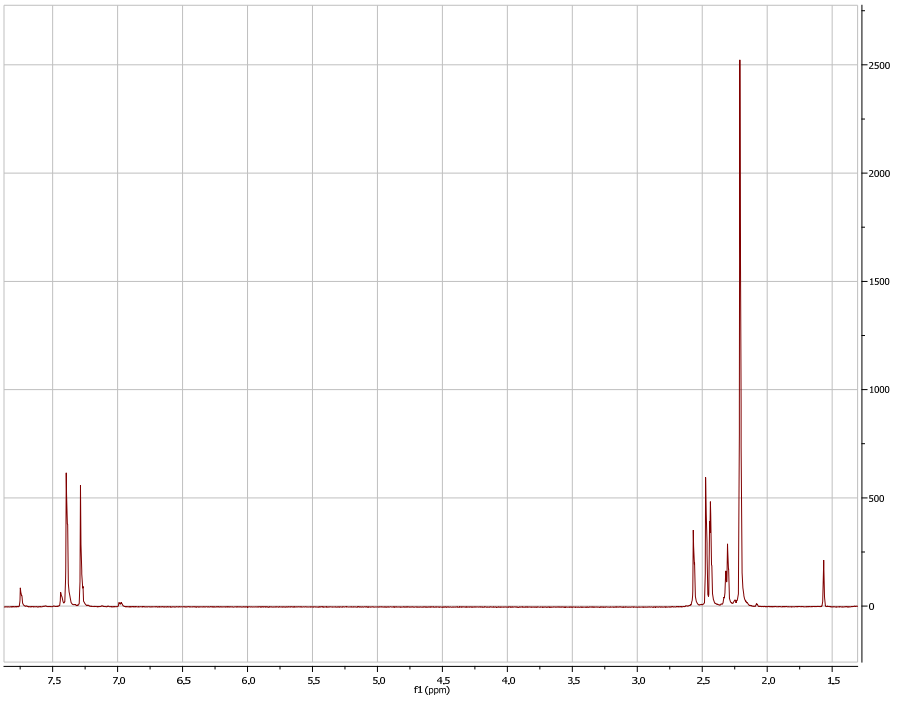
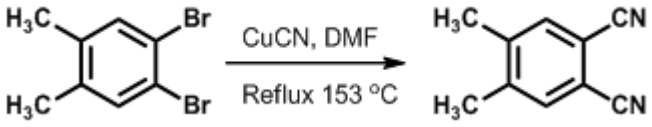


Figure 2: ^{1}H NMR confirmation of the presence and purity of dibromo_o-xylene.

Problems:

The dropper funnel with bromine tends to clog, making the slow, consistent addition of the molecule difficult to maintain. Several times the reaction was attempted, the dropper was checked within the first 15 minutes, found to be clogged, and the valve further opened. Sometimes this caused the Br_2 to add too quickly after it started dripping again which was usually too fast for the reaction to go forward. Also, when the slushy compound was heated and placed in the fridge and crystals didn't form, this process was repeated with about 12 drops of hexane, which sometimes made no difference. This could be because the compound was heated to a temperature which caused it to break down.

The second reaction in the scheme is the formation of dicyano_o-xylene by replacing the adjacent bromine attachments on the benzene ring with CN^-.



The reaction flask was kept under a vacuum for 2 h, after which the reactants were added: 963 mg (11.36 mmol) dibromo_o-xylene, 5.09 g (56.83 mmol) CuCN, 536 µL (6.65 mmol) pyridine, and 50 mL DMF. The DMF was purged with Ar and the reaction was refluxed at 150°C under vacuum for 20 h. It is important not to increase the temperature past 150°C because the solvent starts to break down into amines past these conditions.

Workup:

1. Water Wash:

A solution of 25% ammonium hydroxide is made from stock of 29% NH_4OH by mixing 86 mL 29% NH_4OH with 14 mL DH_2O in a graduated cylinder, which is then transferred to a flask. The NH_4OH is for attracting the left-over Cu ions after CN^- has replaced Br on the aromatic ring. The crude

solution is transferred to the flask with the mixture and the RB is rinsed with a solution of undistilled chloroform and water which dissolves the compound stuck to the sides of the reaction flask. This solution is then transferred to the separatory funnel and rinsed with DMF. The separatory funnel is shaken and the organic layer collected (which includes the chloroform because this is more dense than water). When the aqueous ammonium hydroxide was mixed with the crude product, the solution became blue due to Cu reacting with NH_4^+. The upper, aqueous layer with the excess Cu ions was collected in a waste flask. This washing process was repeated 3 times in order to remove all excess $[Cu(NH_4)_4(H_2O)_n]SO_4$.

Next, 40 mL DH_2O was mixed with a small amount of undistilled chloroform, which was then added to the separatory funnel containing the compound sans $[Cu(NH_4)_4(H_2O)_n]SO_4$. The solution was shaken gently to as to prevent emulsification, and the bottom (organic) layer was collected over anhydrous Na_2SO_4, which separates any remaining water in the organic layer. The top (water) layer was discarded.

2. Evaporation:

The DMF/chloroform solvent mixture is evaporated from the compound by a two-step rotovap process, where first the chloroform is evaporated at a lower temperature, and then the temperature is increased to evaporate the DMF. After this process the product was still in solution, possibly due to pyridine, so the product is gently transferred to a petri dish to evaporate the remaining solvent overnight. The solids that form from evaporation of DMF and chloroform are rinsed/dissolved with DCM, which is then evaporated as well. This solvent was used due its low boiling point.

3. Recrystallization:

The dried product is transferred to a round-bottom flask and the recrystallization process is set up using fluted filter paper, a glass funnel and another Erlenmeyer flask. The funnel is suspended above the flask with a wooden holder in order to allow for air circulation. The dry compound is then mixed with a minimal amount of toluene. This solvent is used because the dicyano_o-xylene is soluble in toluene only at high temperatures. The filter paper, flask, funnel, and compound are all heated with a heat gun – the compound is swirled when heated. The hot compound is then poured into the hot filter paper/funnel, and solution drains and cools, recrystallizing out of toluene solution with decreasing temperature. The product was confirmed with NMR spectroscopy:

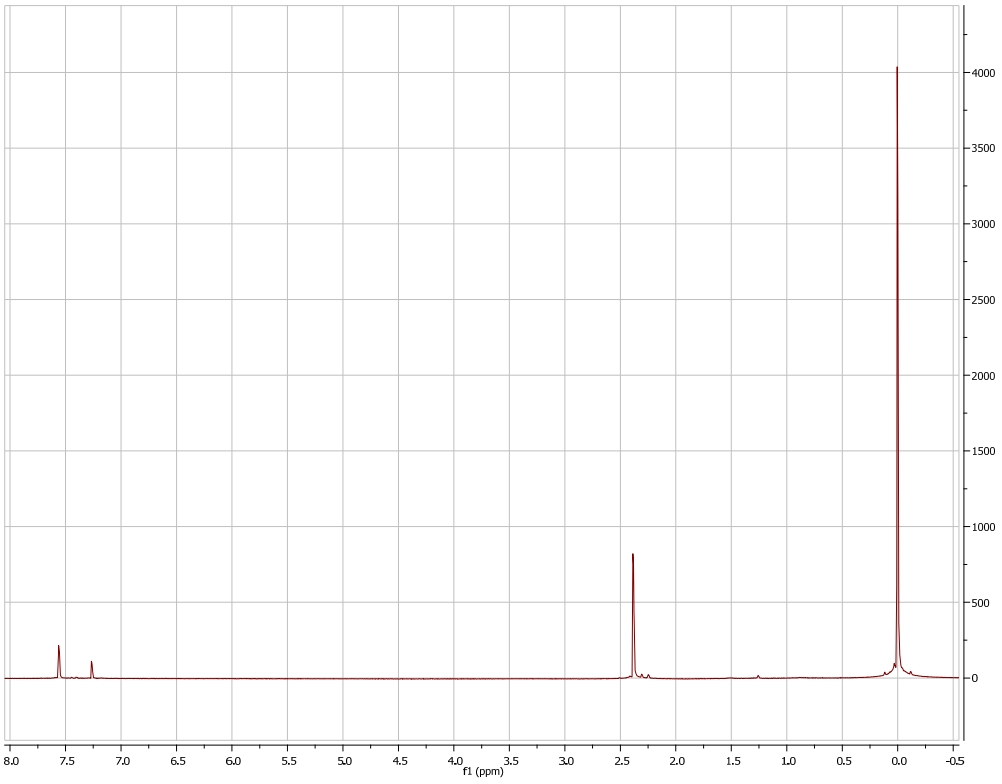


Figure 3. ^{1}H NMR confirmation of the presence and purity of dicyano_o-xylene.

Problems:

The compound with solution after the water wash is supposed to be a pale yellow, but sometimes our solution came out pink due to Cu ions left in solution after the water wash. When this was the case, the process was repeated to be sure that all Cu ions have been separated from the compound and the solution came out yellow. Also, when the product was mixed with toluene and heated for the recrystallization, it was almost brown. After drying and cooling, the color came closer to yellow with a green tint, and still dark. Due to this color (which could come from any number of contaminants and excess reactants) we repeated the recrystallization process.

Molecular photovoltaics is a useful and promising research outlet as technology continually shrinks in size and different avenues of renewable energy are explored. This paper summarizes the first two steps in the reaction scheme shown above. The reactions took much longer than planned because I had little background knowledge in the set-up and execution of the different types of reactions, purification techniques, and spectroscopic analyses.

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References

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